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VAPOR-PHASE INFRARED ABSORPTIVITY COEFFICIENT OF CYCLOHEXYL METHYLPHOSPHONOFLUORIDATE

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14. ABSTRACT
We measured the vapor-phase absorptivity coefficient of cyclohexyl methylphosphonofluoridate (GF), a chemical warfare agent, in the mid-infrared (4000-550 cm^{-1}) at a spectral resolution of 0.125 cm^{-1}. The GF used in the feedstock was purified by fractional distillation and analyzed by NMR and gas chromatography-mass spectrometry to verify its purity. In this report, we describe the experimental method used to acquire the individual spectra that produced the composite spectrum, summarize the statistical uncertainties in the data, and provide a comparison to similar data from another laboratory.

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EXECUTIVE SUMMARY

We measured the vapor-phase absorptivity coefficient of cyclohexyl methylphosphonofluoridate (GF, Cyclosarin) in the mid-infrared. We used agent filled saturator cells suspended in a temperature controlled liquid bath to generate continuous streams of the compound diluted in nitrogen, which were sent to a variable path White cell and measured using a high resolution research grade Fourier transform infrared spectrometer. The purity of the feedstock was verified by nuclear magnetic resonance spectroscopy and gas chromatography-mass spectrometry. The mass of GF in the vapor was determined with a gravimetric method, and the vapor purity was verified with thermal desorption gas chromatography. Fourteen spectra at different concentration-pathlength products were processed line by line through least squares analysis using MatLab to produce the absorptivity coefficient of the compound and the statistical uncertainty in the data. Uncertainties in the data, expanded to a confidence interval of 2σ ($P = 0.95$), are Type-A: 3.6% and Type-B: 3.4% of the absorptivity coefficient. We report a comparison of our data to that obtained by another laboratory using a different vapor generation method.

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PREFACE

The work described in this report was performed under the direction of the Detection Capability Officer, Defense Threat Reduction Agency Joint Science and Technology Office. This work was started and completed in November 2006.

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Acknowledgments

The authors thank Dr. Frederic J. Berg and Leslie McMahon, Chemical Sciences Division, for their work in preparing the feedstock material used in these tests at a purity of >99%. Their diligent efforts enabled us to obtain spectral data of the highest possible quality.

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VAPOR-PHASE INFRARED ABSORPTIVITY COEFFICIENT OF CYCLOHEXYL METHYLPHOSPHONOFLUORIDATE

1. INTRODUCTION

We measured the high resolution vapor-phase absorptivity coeffieient of the nerve agent, eyelohexyl methylphosphonofluoridate (GF) in the speetral range of 4000-550 em^{-1}, at a speetral resolution of 0.125 em^{-1} in units of $(\mu mol/mol)^{-1}m^{-1}$ and eomputed the uncertainties in the data. Previous efforts at the U.S. Army Edgewood Chemieal Biologieal Center (ECBC) to obtain the absorptivity eoeffieients of this eompound dating baek to the 1960's were performed at lower resolution on a grating spectrometer.[1] Given the extensive use of vapor-phase infrared speetra for standoff deteetion of ehemieal warfare agents (CWAs), the need for eurrent data is thus apparent.

Cyclohexyl methylphosphonofluoridate has the Chemieal Abstraets Serviee (CAS) Registry Number 329-99-7 and is indexed under the name: phosphonofluoridic aeid, methyl-, eyelohexyl ester. The moleeular formula is $C_7H_{14}FO_2P$ and its formula weight is 180.16. Other synonyms for the eompound inelude Cyelosarin, methyl eyclohexyl phosphonofluoridate, eyelohexyl methylfluorophosphonate, and EA-1212. The strueture is shown in Figure 1.

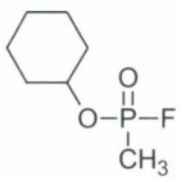

Figure 1. Strueture of GF

Cyelohexyl methylphosphonofluoridate is a nerve agent that was first synthesized in Germany during WWII although it was not employed in eombat during WWII. The vapor pressure of the eompound at several temperatures is 7.36 Pa, 0.055 Torr (20 °C); 11.2 Pa, 0.084 Torr (25 °C); and 101325 Pa (228.7 °C, ealculated boiling temperature).[2]

2. EXPERIMENTAL PROCEDURES

2.1 Instrumental Details.

The system used to generate the eontinuous vapor stream was an adaptation of the saturator eell method developed at ECBC for measuring the volatility of CWA related compounds.[3]

The method, modified to generate eontinuous streams of ehemieal eompounds for obtaining quantitative vapor-phase infrared speetra, has been used to measure the absorptivity

coefficients of benzene[4] as well as a variety of CWA related compounds.[5,6,7,8] The experimental setup, data collection, and post-processing are described in more detail in ECBC-CR-076 and SOAR-07-20.[4,5] The saturator passes a stream of nitrogen carrier gas, obtained from the boiloff of a bulk liquid nitrogen tank, across a cylindrical alumina wicking mechanism closed at one end in a glass holder filled with the analyte. A saturated vapor-liquid equilibrium of the analyte on the downstream side of the saturator cell results with the concentration of the analyte determined by the temperature of the liquid phase. By suspending the saturator cell in a constant temperature bath, the concentration of the analyte can be predicted by its vapor pressure at the temperature of the bath.

The apparatus used in the Quantitative Fourier Transform Infrared (FTIR) Laboratory uses Brooks Model 5850S mass flow controllers to maintain a constant flow to the saturator cell, along with a second mass flow controller to add diluent to the stream, providing an additional means of adjusting the concentration of the compound delivered to the White cell of the FTIR. Linearity of the S series mass flow controllers is adjusted using a second order polynomial, resulting in uncertainties of approximately 1% or better of rate at flows ≥25% of full scale.

Spectra were obtained with a Bruker Model IFS/66V FTIR. The instrument is equipped with both deuterated triglycine sulfide and mercury-cadmium-telluride (HgCdTe) detectors and is capable of obtaining spectra with a maximum spectral resolution of 0.1125 cm^{-1} (unapodized). The interferograms were recorded from 15798-0 cm^{-1} with a resolution of 0.125 cm^{-1}. Absorbance (log base-10) spectra were processed with boxcar apodization and 2X zero filled to obtain a data spacing of 0.0625 cm^{-1}. The instrument is equipped with a variable path White cell. The experimental data used path lengths of 4.057, 5.377 and 8.024 m. The temperature of the White cell was maintained at 23 ± 0.1 °C by using a thermostatically controlled chamber enclosing the spectrometer and cell. Data were acquired at a speed of 60 KHz (HeNe laser zero crossing frequency) using the HgCdTe detector. The ratios between the single beam spectra of the CWA and the spectra of clean, dry nitrogen were computed. To minimize the effects of nonlinearity in the detector, the interferograms were processed using the proprietary Opus nonlinearity correction function. All interferograms were archived enabling further post-processing of data.

Temperature and pressure data were recorded using National Institute of Standards and Technology traceable digital manometers and thermometers, and all data were archived. Concentration-pathlength products (CL) were computed in units of µmol/mol(m) (ppm-m). A differential pressure manometer had previously been used to measure the dynamic pressure in the White cell with gas flowing into the cell and the ambient pressure was plotted versus the differential pressure. The resulting equation was used to correct the readings from the ambient pressure manometer to the pressure in the White cell. The concentration-pathlength data were corrected to 296 K and 1.0132×10^5 Pa (760 Torr) using the ideal gas law.

2.2 Feedstock.

The material used to generate the vapor streams for the experiments was purificd by fractional distillation to remove the stabilizer. The purity was determined to be: >99.9 mol% (^{31}P nuclear magnetic resonance spectroscopy, NMR); and 99.6% (gas chromatography-mass spectrometry, GC-MS), with 0.4% dicyclohexyl methylphosphonate. The latter impurity, because of its low vapor pressure relative to that of the GF, would not be expected to be observed in the effluent. Sampling of the vapor effluent by thermal desorption-GC with a flame ionization detector indicated a purity of 99.6%. The spectra of the vapor from the saturator cell showed the presence of both water vapor and hydrogen fluoride in the effluent at a combined mass concentration that ranged from 1.4 to 0.2% during the first day's run. Thereafter, only trace concentrations of these two impurities were observed in the vapor. With the exception of the first day's trial, we used a mass concentration of 99.8 ± 1.0% to compute the CL of the vapor.

3. RESULTS AND DISCUSSION

Threc trials were run to obtain spectra at 14 CL with a 39 to 401 μmol/mol(m) range after corrccting for pressure and temperature variations. A trial is defined as filling and weighing the saturator cell, suspending it in the bath, applying a stream of nitrogen for a measured time, acquiring several spectra, stopping the nitrogen and removing it from the bath, and reweighing the saturator cell after drying the exterior surfaces and re-equilibrating to room temperature.

Vapor generation was done with the saturator cell suspended in a water bath maintained at 22.5, 23, or 24 °C. The initial spectra obtained appeared to be contaminated by water vapor and HF. This was confirmed by matching to the quantitative vapor-phase infrared database from Pacific Northwest National Laboratory (PNNL).[9]

The absorptivity coefficients of both impurities arc available in the PNNL database and were used to compute the contribution of these compounds to the mass loss in the saturator ccll. The concentration of the impurities was determined by first using spectra subtraction to remove the features of the impurity from the contaminated spectrum. Thc difference in the integrated areas of the uncorrected (minuend) and corrected (difference) spectra was presumed to be the contribution of the impurity to the spectrum:

$$\int S_{unc} - \int S_{corr} = \int S_{impurity} \tag{1}$$

The absorptivity coefficient spectra are provided in units of [μmol/mol(m)]$^{-1}$; thus, the concentration of the respective contaminants in the GF could be computed by using Beer's Law:

$$c = \frac{A}{\alpha b} \tag{2}$$

where c is the concentration of the impurity in μmol/mol, $A = \int S_{impurity}$, α = the integrated area of the reference spectrum of the impurity, and b = the pathlength at which the GF spectrum was obtained. The reference spectra were recorded at a reference temperature of 296K and 101320 Pa, and the concentrations obtained with eq 2 were corrected for deviations from that temperature and pressure using the ideal gas law. The mass rate, R, of the compounds in the vapor stream in mg/min was then calculated using eq 3:

$$R = \frac{c \times mw \times flow}{24150} \tag{3}$$

where mw = the mass of 1 μmol of the impurity, and $flow$ = the total flow rate of carrier and diluent in liters per minute. The bottom of the right side of eq 3 incorporates factors for the molar volume of nitrogen at 296 K (24.15 L) and the conversion from micrograms to milligrams.

The mass rate of water vapor decreased during the first day's run from 1.3 to 0.1% of the total mass in the vapor stream and remained at 0.1% for the subsequent experiments. The mass rate of HF was constant at 0.1% of the total mass. We used a purity of 99.8 ± 1% to compute the contribution of GF to the vapor. The expanded uncertainty of 1% applied to the purity of the vapor may be conservative. The absorptivity coefficient of the GF was computed using $\int_{corr}$, i.e., the spectra from which the features of the impurities had been removed by spectral subtraction. Before computing the absorptivity coefficient, baseline corrections of the spectra were performed with a multipoint linear subtraction. The corrections in no case exceeded 0.001 A.

As an initial check of the quality of the data, Beer's Law plots of two spectral lines, 1022.4 and 2949.6 cm^{-1}, were calculated using MatLab. At least for these two spectral lines, the data appeared to be well fitted, with no points lying outside the 95% confidence limits for either a repeated set or a repeated single x or the 95% confidence limits for a Grubbs Test for Outliers (Figures 2 and 3).

The absorptivity coefficient (α), along with the Type-A statistical uncertainties, was computed line by line within the full spectral range of 4000-550 cm^{-1}. Figure 4 shows the computed absorptivity coefficient in $(\mu mol/mol)^{-1}m^{-1}$, along with the Type-A statistical uncertainties (2σ). Multiply α shown by 0.1340 (eq 4) to obtain values in $(mg/m^2)^{-1}$.

$$\frac{m^2}{mg}\left(\frac{24.15}{mw}\right) = \frac{mol}{\mu mol(m)} \tag{4}$$

The absorptivity coefficient and statistical uncertainty were computed line by line using a MatLab program written in-house. Values of ($A = -\log T$) > 1.5 are normally assigned a weight of zero. Because all values recorded were for $A \leq 0.973$, all data were weighted at 1. Computed absorptivity coefficients for spectra (recorded by PNNL) used a least squares weighted according to $T_i^2(v)(A = -logT)$.[9] We discuss our reasons for using an unweighted technique in more detail in ECBC-CR-076.[4] We have additionally shown that the signal-to-noise

ratio of our system with a White cell path length typically used in our measurements reaches a maximum value at approximately 0.4 to 0.5 *A*. Because most data, except for the most intense absorption features, are generally recorded at absorbance values <0.5, we see little or no value in using a weighted least squares technique.

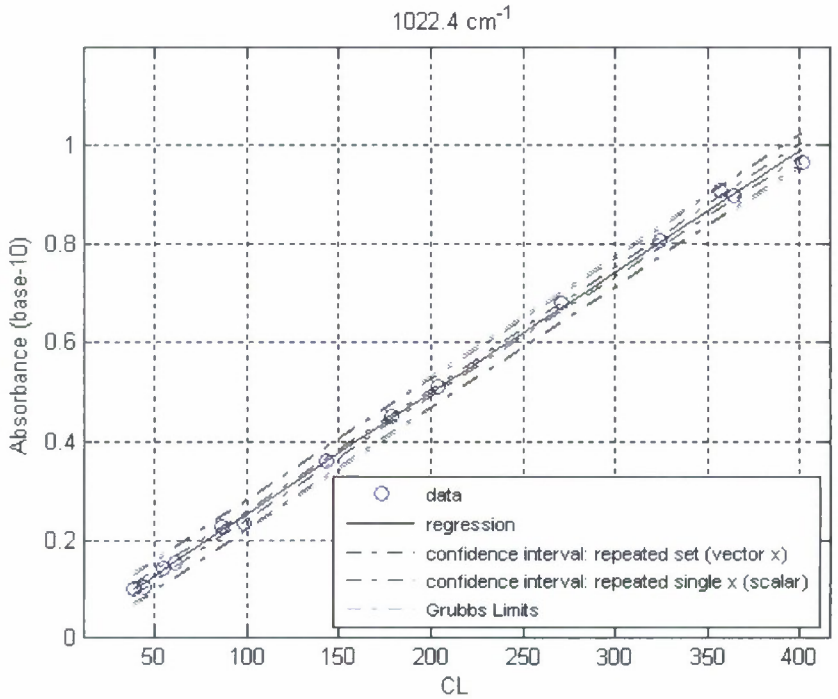

Figure 2. Beer's Law Plot of 1022.4 cm^{-1} Line in Vapor-Phase Spectrum of GF

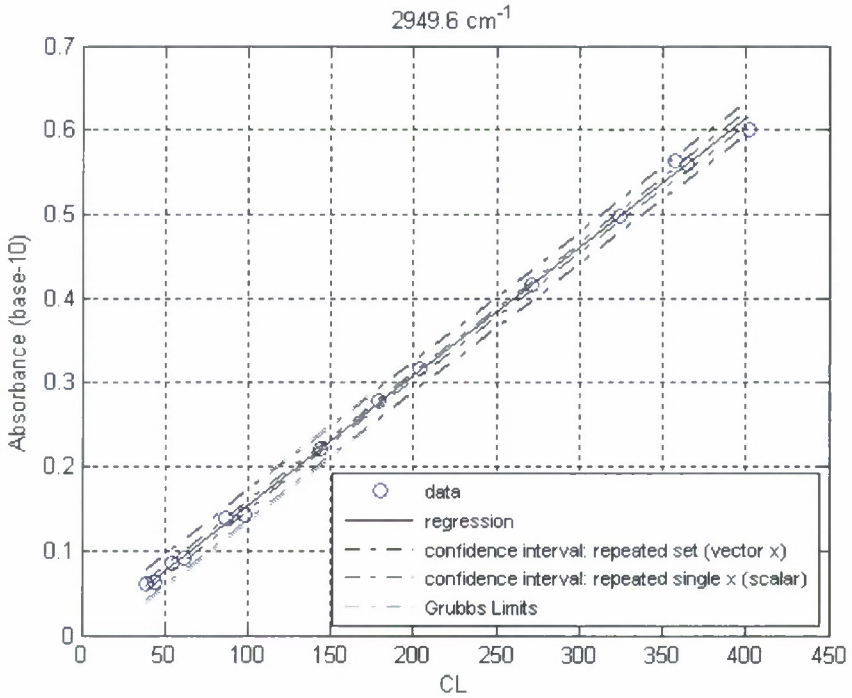

Figure 3. Beer's Law Plot of 2949.6 cm^{-1} Line in Vapor-Phase Spectrum of GF

Table 1 provides the absorptivity coefficients in $(\mu mol/mol)^{-1}m^{-1}$ and $(mg/m^2)^{-1}$ for selected bands in units of wavenumber and micrometers.

Table 1. Absorptivity Coefficient of GF for Selected Bands

$\tilde{\nu}$ /(cm^{-1})	2949.59	1301.655	1022.329	931.7509
λ/μm	3.390301	7.682527	9.781591	10.73248
$(\mu mol/mol)^{-1}m^{-1}$	1.541E-03	9.590E-04	2.475E-03	8.838E-04
m^2/mg	2.042E-04	1.271E-04	3.281E-04	1.172E-04

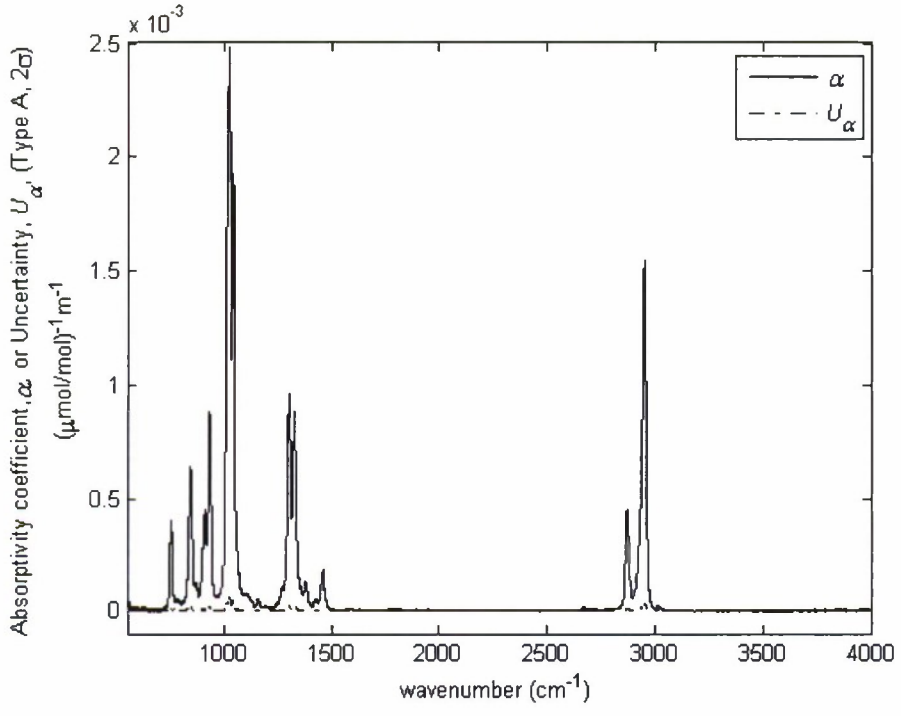

Figure 4. Absorptivity Coefficient and Statistical Uncertainty (Type-A, 2σ) of GF

In general, expanded Type-A uncertainties were 2 to 2.5% of the absorptivity coefficient (Figures 5 and 6). Figure 5 is a plot of absorptivity coefficients (abscissa) and fractional uncertainty (Type-A, U_A, 2σ) (mantissa). Figure 6 is a plot of the absorptivity coefficient and uncertainty and it includes a best fit of the data points obtained by least squares, which is an approximation of $U_A \approx ax + b$. For the fitted line in Figure 6 the coefficients are $a = 2.10 \times 10^{-2}$ and $b = 1.82 \times 10^{-6}$ (Table 2).

Table 2. Type-A Statistical Uncertainty for GF Vapor-Phase Absorptivity Coefficient

Type-A Uncertainty $2\sigma \approx ma + b$	
Slope m	Intercept b
2.10×10^{-2}	1.82×10^{-6}

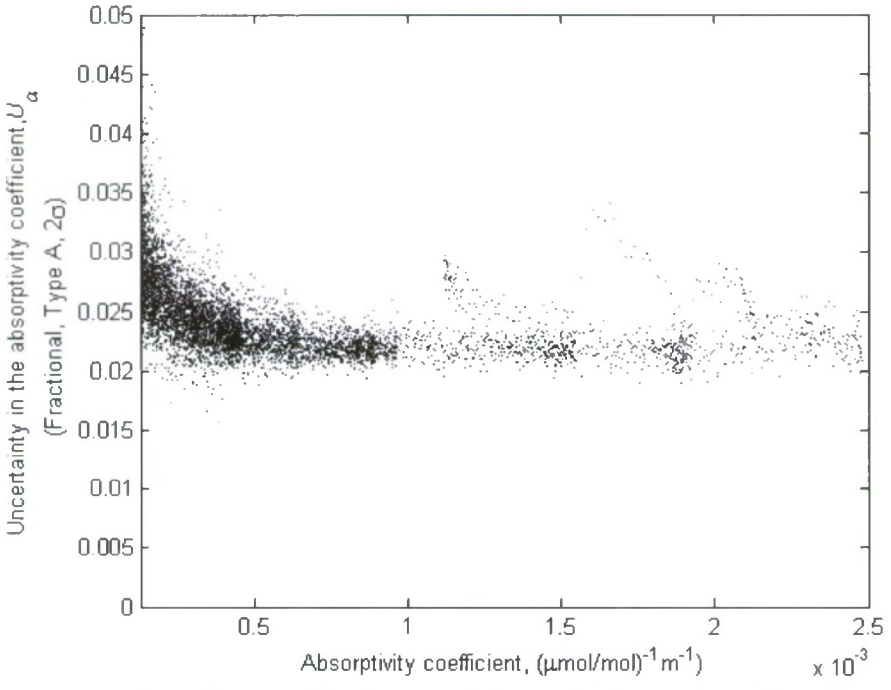

Figure 5. Absorption Coefficient (Abscissa) and Type-A Uncertainty (Fractional, 2σ) for GF

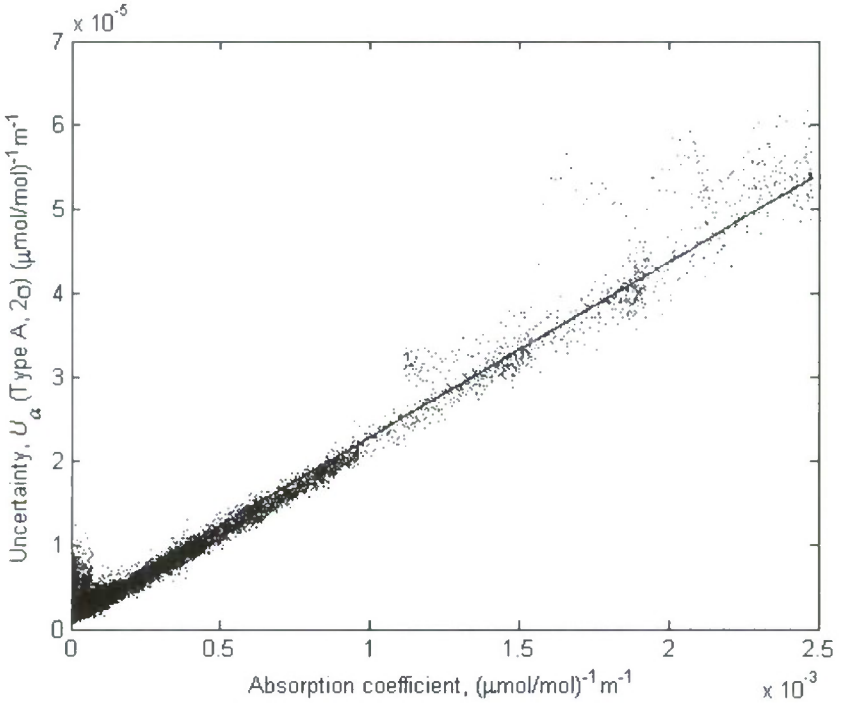

Figure 6. Absorption Coefficient (Abscissa) and Type A Uncertainty (2σ) for GF. The line indicates the "best fit" obtained by least squares.

Type-B estimated standard errors, along with their sources, as well as the combined Type-A and B uncertainties are provided in Table 3. The expanded combined Type-B uncertainty was computed using eq 5:

$$\Delta_B = (\Delta L^2 + \Delta T^2 + \Delta P^2 + \Delta FTIR^2 + \Delta NL^2 + \Delta MR^2)^{1/2} \times 2 \quad (5)$$

The sources of uncertainty and their fractional values, as well as an explanation of the symbols in eq 1 are given in Table 4. The Type-A uncertainty of 3.6% (2σ) indicated in Table 3 is valid for values of the absorptivity coefficient ≥ 0.000124 $(\mu mol/mol)^{-1}m^{-1}$ ($\alpha \geq 5\%$ of the peak of maximum intensity). For absorptivity coefficients ≥ 0.000372 $(\mu mol/mol)^{-1}m^{-1}$ (all of the major absorption bands in the fingerprint region), the Type-A uncertainty averages 2.5% of the absorptivity coefficient.

Table 3. Uncertainties in Absorptivity Coefficient of GF from ECBC Data where $\alpha \geq 0.000124$ $(\mu mol/mol)^{-1}m^{-1}$

Symbol	Fractional deviation	Source
ΔL	0.005	Pathlength
ΔT	0.0006	Temperature of White cell
ΔP	0.0003	Pressure
$\Delta FTIR$	0.0005	Drift in spectrometer
ΔNL	0.01	Nonlinearity in detector
ΔMR	0.005	Mass rate
ΔD	0.01	Dilution rate
$\Delta purity$	0.005	Purity of vapor
Δ_B	0.034	Combined type B (2σ)
Δ_A	0.036	Type-A deviation (2σ)

4. INTERLABORATORY COMPARISON

Comparison of data between laboratories, especially when obtained using different methods, can be useful in assessing the experimental methods and for validating the accuracy of the data. One other source for the high resolution absorptivity coefficient of cyclohexyl methylphosphonofluoridate for comparison to the data acquired at ECBC is that obtained by Pacific Northwest National Laboratory (PNNL) at Dugway Proving Ground.[9] The PNNL database includes a detailed discussion of experimental methods and statistical processing. Each absorptivity coefficient spectrum is provided with a metadata file listing physical data for the compound, temperature and pressure range, number of individual spectra included in the fit of the absorptivity coefficient, and Type-A and Type-B uncertainties.

As can be seen in Figure 7, the absorptivity coefficients from ECBC and PNNL are qualitatively similar. The metadata file associated with the PNNL spectrum indicates uncertainties of 3.1% (Type-A) and $\leq 10\%$ (Type-B). A comparison of the data from the two laboratories (Table 4) shows that in the range from 4000 to 550 cm^{-1}, the PNNL integrated absorptivity coefficient is ~10.2% higher than ours.

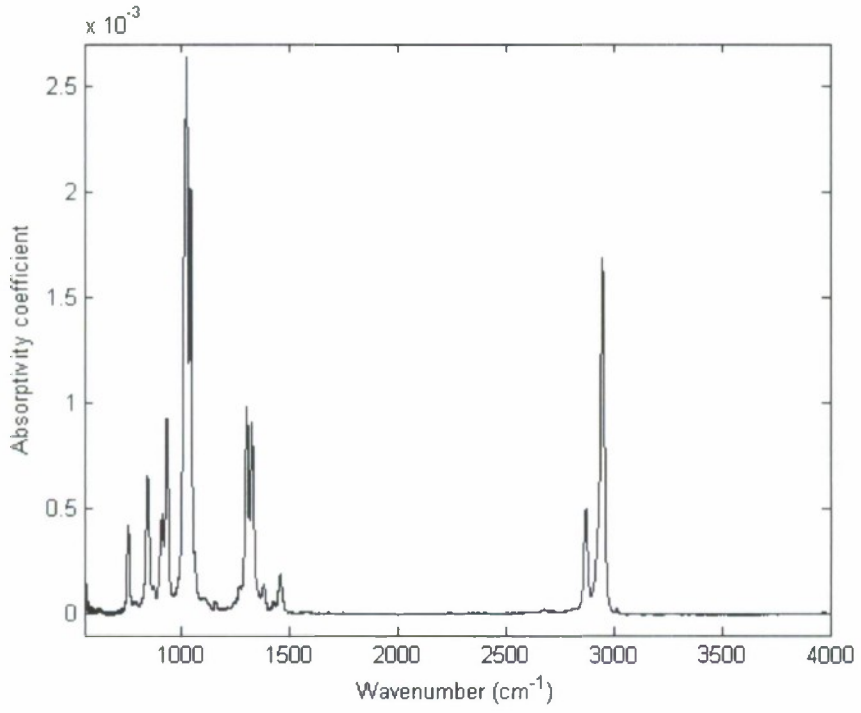

Figure 7. Absorptivity Coefficient of Vapor-Phase GF from PNNL. The spectrum is qualitatively similar to that obtained in our laboratory (Figure 4).

The differences in the two spectra across different regions are more remarkable, however, with the Δ as large as 18.5% in the vicinity of 3000 cm^{-1}. This is attributable, at least in part, to differences in the baselines of the two spectra, most readily observable within the region associated with CH stretch (Figure 8). In general, across the entire spectral range, the baseline of the PNNL spectrum appears to be shifted on the lower frequency ("red") side of absorption features. While this may in part arise from the seventh order polynomial baseline subtraction used to correct the PNNL spectrum, we believe this is more likely the effect of scattering from aerosols present in the vapor of the spectra used to compute the composite spectrum. The residual spectrum was obtained by subtracting the ECBC spectrum from the PNNL spectrum.

Table 4. Comparison of Integrated Absorptivity Coefficients of GF from PNNL and ECBC

Integrated Absorptivity Coefficient			
Range/cm^{-1}	PNNL	ECBC	(ECBC-PNNL)/ECBC X 100 (%)
4000-550	0.2790	0.2532	-10.2
3153-2496	0.06146	0.05187	-18.5
1633-552	0.2135	0.1973	-8.2

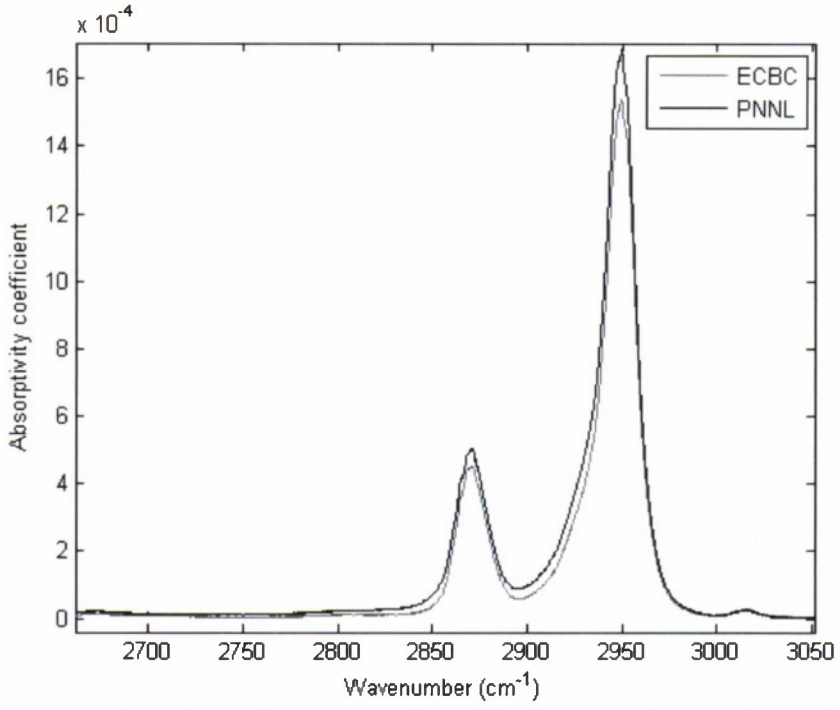

Figure 8. Absorptivity Coefficient Spectra of GF in Vicinity of 3000 cm^{-1} from ECBC and PNNL. The PNNL spectrum appears to exhibit a baseline shift on the lower frequency side of the peaks associated with CH stretch. This may be indicative of aerosol scattering in the PNNL spectrum.

Figure 9 shows the residual spectrum overlaid with the ECBC vapor spectrum and the PNNL liquid absorptivity coefficient spectrum. The arrows within the figure indicate the presence of several features, which appear to be consistent with liquid GF as well as other bands that may arise from impurities. The aerosols are likely caused by the syringe pump method used to generate the vapor used for the PNNL spectra. The apparent presence of the liquid in the PNNL spectrum, combined with the effects of aerosol scattering effects on the baseline and possible impurities, renders a quantitative comparison of the vapor spectra from the two laboratories difficult at best.

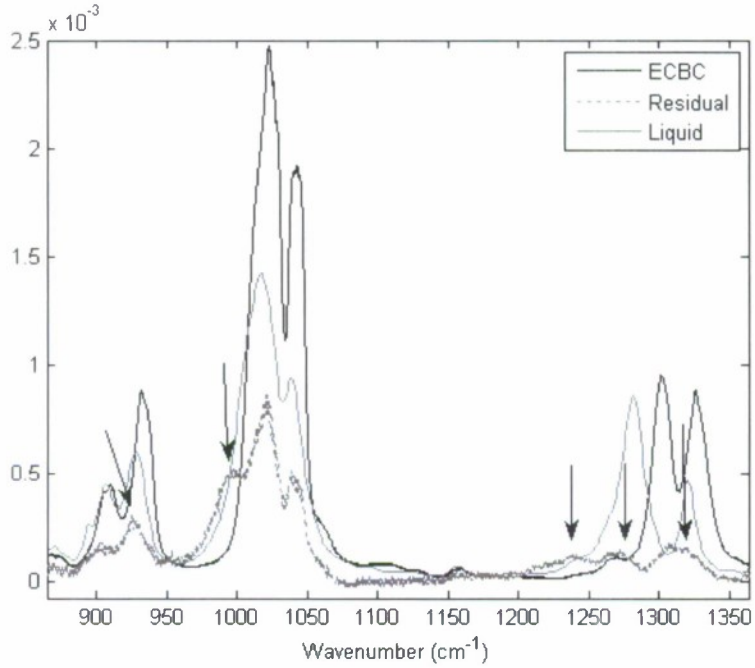

Figure 9. Absorptivity Coefficient Spectra of GF from ECBC (Vapor) and PNNL (Liquid) and Residual Spectrum Obtained by Subtracting ECBC Vapor Spectrum from PNNL Vapor Spectrum. The arrows indicate the presence of absorption features in the residual that are apparently associated with a combination of liquid-phase GF and impurities present in the vapor used to generate the PNNL vapor-phase spectrum.

5. CONCLUSIONS

We used a saturator cell system to acquire vapor-phase spectra of the nerve agent, cyclohexyl methylphosphonofluoridate (GF). These spectra were then used to compute the vapor-phase absorptivity coefficient at 0.125 cm^{-1} resolution. Uncertainties are Type-A = 3.6% and Type-B = 3.4% of the absorptivity coefficient for features ≥5% of the peak of maximum intensity. The integrated absorptivity coefficient obtained by ECBC is 10.2% lower than that obtained by PNNL. A comparison of the spectra from the two laboratories indicates the presence of absorption features from aerosols or impurities in the PNNL spectrum, which render a more precise comparison difficult.

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